AD-A077 366   NAVAL RESEARCH LAB WASHINGTON DC   F/G 13/10
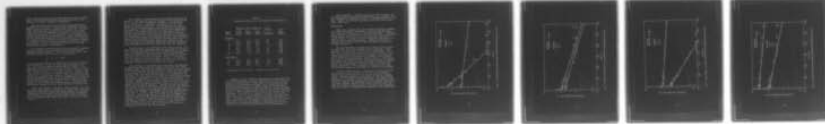   THE EFFECT OF PRESERVATIVE SOLUTIONS ON HULL PLATE SAMPLES FROM--ETC(U)
               NOV 79 R N BOLSTER
UNCLASSIFIED   NRL-MR-4117   NL

| OF |
AD-
A077366

END
DATE
FILMED
1 -80
DDC

The Effect of Preservative Solutions on Hull Plate Samples from the USS MONITOR

ROBERT N. BOLSTER

Surface Chemistry Branch
Chemistry Division

LEVEL

November 20, 1979

DDC

NOV 28 1979

A

79 11 28 051

NAVAL RESEARCH LABORATORY
Washington, D.C.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 4117	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE EFFECT OF PRESERVATIVE SOLUTIONS ON HULL PLATE SAMPLES FROM THE USS MONITOR.		5. TYPE OF REPORT & PERIOD COVERED Final report on an NRL problem.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert N. Bolster		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem 61C02-04.402
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE Nov 1979
		13. NUMBER OF PAGES 19
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This study was undertaken at the request of the Division of Archives and History, North Carolina Department of Cultural Resources and the Office of Coastal Zone Management, National Oceanic and Atmospheric Administration.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

MONITOR	Chloride extraction
Preservation	Marine archaeology
Corrosion	Stabilization
Corrosion inhibition	Rust inhibition

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The temporary preservation of artifacts recovered from the USS MONITOR are described. An alkaline solution of sodium benzoate with biocide was effective in preserving a section of wrought iron hull plate for many months. The effects of several preservative solutions on small sections of MONITOR hull plate were studied. Sodium benzoate and nitrite were found to be effective with trisodium phosphate, but ineffective in the absence of an alkaline pH buffer. Chloride seawater salts were extracted at rates conforming to first-order kinetics. However, extraction was not

(Continues)

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

i

20. Abstract (Continued)

complete under static conditions, and additional chlorides appeared upon exposure of the specimens to humid air. Descaled specimens were more stable in the atmosphere than those with the scale intact.

ii

CONTENTS

iii

THE EFFECT OF PRESERVATIVE SOLUTIONS ON HULL
PLATE SAMPLES FROM THE USS MONITOR

INTRODUCTION

In August, 1977, a joint expedition by the Harbor
Branch Foundation, National Oceanic and Atmospheric Adminis-
tration, North Carolina Division of Archives and History,
and the U. S. Navy to the wreck of the USS MONITOR recovered
a loose section of the hull plating, a brass lantern found
near the wreck, and a camera system which was lost by an
expedition four years earlier. All of these were brought
to the Naval Research Laboratory (NRL) for temporary pre-
servation and preliminary examination. The wrought iron
plate was roughly "L"-shaped, weighed 27 kg (60 lb), and
measured 106 x 134 cm (42 x 53 in). It was severely corroded,
the missing portions apparently having been destroyed by cor-
rosion. Most of the surface was covered with scale and mar-
ine growth. The lantern, 46 cm tall and 18 cm in diameter
(18 x 7 in), appeared to be in relatively good condition,
although the thin sheet metal parts were destroyed or per-
forated in places. Both artifacts had been kept wet during
their transportation to NRL. The temporary preservative
treatments employed during their stay at NRL are described
below.

Ferrous metal objects recovered after lengthy immersion
in the sea are not stable in the atmosphere, as the chloride
ions present promote continued corrosion. Stabilization can
be accomplished by hydrogen reduction or electrolysis, but
for objects the size of the MONITOR or its parts, these pro-
cedures may not be feasible. Leaching in a preservative
solution, with or without descaling, is an alternative com-
monly used by conservators. Such solutions are also useful
for the temporary preservation of recovered artifacts pend-
ing further treatment. The solution chosen by the author
for temporary preservation of the plate gave satisfactory
results, but there was no opportunity to study the effects
of different inhibitors, various concentrations, and the
influence of pH. When samples were cut from the plate in
June 1978, one sample was requested for a limited evaluation
of preservative treatments.

1

TEMPORARY PRESERVATION OF THE ARTIFACTS

The wrought iron hull plate was kept immersed in tap water in a wooden crate lined with polyethylene film and padded with bubbled polyethylene packing material. To inhibit corrosion, 1% by weight of sodium benzoate was dissolved in the water, and the pH was kept between 7 and 10 (slightly alkaline) by the addition of sodium carbonate and sodium hydroxide. These materials were selected because of their known effectiveness in inhibiting the corrosion of ferrous metals in water, minimal interference with later treatment, analysis, or examination of the plate, and low toxicity. This treatment appeared to be effective in preventing further rusting of the exposed metal or exfoliation of the scale.

A few days after the plate was received, a dark stain appeared and spread until, in two weeks, the entire plate was darkened. This was apparently due to sulfidation resulting from the bacterial decomposition of the marine growth. The Marine Biology and Biochemistry Branch of NRL recommended the addition of "Sodium Omadine" (sodium 2-pyridinethiol-1-oxide). This biocide, added to a concentration of 1.5 parts per million, kept the slime and bacterial growth under control, although the solution still darkened with time.

The plate was stored in this manner at NRL for seven months, the solution being replaced three times, and receiving additional sodium hydroxide nine times. During this period the plate was photographed, weighed, measured, and radiographed; and discussions were held to determine the number and location of samples to be cut from it for further study.

The brass lantern was similarly placed in a crate lined with polyethylene bags and filled with tap water. A trace of sodium carbonate was added to prevent the water from becoming acidic, and 1 ppm of the biocide was added to inhibit slime growth. After three weeks at NRL, the lantern was transferred to the Smithsonian Institution's Conservation and Analytical Laboratory. No changes in its condition were observed during this period.

EXPERIMENTS WITH SAMPLE 0408 - PROCEDURES

Sample 0408 from the MONITOR hull plate was 8 x 2 in (20.3 x 5.1 cm), the length parallel to the longer dimension of the plate, and the center 13 cm (5 in) from the longer edge. Judging from the radiographs, the metal thickness in

this area was somewhat greater than average. The sample was weighed and the accretion and scale were scraped from both sides. The sample was then cut into 16 pieces approximately 25 mm square with a bandsaw. These specimens were marked, weighed, and measured.

Seven of the pieces with relatively thick scale remaining on the "up" side were placed in experimental preservative solutions after a brief rinse with distilled water. The remaining nine were further chipped and scraped, and pickled in warm 20% sulfuric acid, inhibited with thiourea, to remove the surface scale and rust. Cleaning was continued until only a few dark areas, presumed to be slag inclusions, remained.

Due to the limited number of specimens available, the study was limited to benzoate and nitrite inhibitors at different concentrations, with and without trisodium phosphate to raise the pH, and a few control experiments without inhibitors. The solutions used are listed in Table 1 along with the identifications of the specimens used. In four cases, the corrosion observed was so severe that the specimens were removed from the original solutions after six days and placed in other solutions, which are listed in the lower part of the Table.

Each specimen was placed in a separate glass weighing bottle having a cover with a ground joint. The volume of the solution used was always 25 ml. Specimens were examined periodically to determine the extent and nature of corrosion occurring, and the solutions were monitored for changes of pH and chloride ion concentration. The pH was measured with a glass electrode and a double juntion reference electrode with 0.1 M KCl in the outer chamber to reduce the amount of chloride added to the solutions by seepage from the electrode. Chloride concentrations were measured with a solid-state specific ion electrode (Orion Research Model 96-17-00). This electrode is sensitive to interference by sulfide ions, a limitation which was encountered with some of the specimens, especially those with scale. A liquid membrane electrode (Orion Research Model 93-17), which is less sensitive to sulfide, was found to be unsuitable due to interference in the nitrite, benzoate, and phosphate solutions. With the solid-state electrode, the interferences were equivalent to 0.3 to 4.7 parts per million (ppm) of chloride, and the data were corrected by subtracting these background levels. The solutions were replaced occasionally to keep the chloride concentrations low.

3

Table 1

Experimental Treatments of MONITOR Hull Plate Specimens

Treatment (Solutions: wt % in distilled water)		Specimen Identification	
		With Scale	Descaled
Sodium benzoate	0.1%	-	1
Sodium benzoate	0.5	7*	2
Sodium nitrite	0.1	-	3
Sodium nitrite	0.5	9	4*
Trisodium phosphate	0.5	10	5
Sodium nitrite trisodium phosphate	0.1 0.5	11	6
Sodium benzoate trisodium phosphate	0.1 0.5	12	8
Distilled water		14*	13*
Ambient atmosphere		15	16

*Transferred after six days to:

Sodium benzoate trisodium phosphate	0.5 0.5	7	13
Sodium nitrite trisodium phosphate	0.5 0.5	14	4

After 119 days (2850 hrs), the specimens in preservative solutions were removed, rinsed, dried, weighed, and placed in a desiccator in an atmosphere maintained at 81% relative humidity to determine their stability. After 15 days, five specimens which showed the presence of deliquescent salts were removed, rinsed, and kept in the ambient atmosphere. The other nine were removed after an additional 28 days and not rinsed. After 200 days under ambient conditions, all 14 were examined again, rinsed and dried. All of these rinses were with 25 ml of distilled water, which was

then checked for chloride content to determine the amount
released by delamination of the scale or the rupture of
salt-containing pockets.

RESULTS

The intact sample weighed 476.9 g (wet). On the "down"
side, the accretion and scale flaked off together easily.
The total weight removed was 32.5 g (dry). The "up" side
accretion came off less readily, and the scale adhered
tightly to the metal. The accretion removed weighed 10.7 g
(dry). The nine specimens descaled lost a total of 19.4 g,
13.2 during chipping and 6.2 during pickling, and the remain-
ing metal weighed 207 g. The derived composition of the
original sample is given in Table 2.

Table 2

Composition of MONITOR Hull Plate Sample 0408

Material	Amount	
	g/cm^2	wt %
Metal	3.6	82.2
"Down" side accretion and scale	0.32	7.3
"Up" side accretion	0.11	2.5
"Up" side scale	0.24	5.5
Adherent scale, both sides	0.11	2.5
	4.38	100.0

The sample was thus approximately 4/5 metal and 1/5 scale
and accretion. The average thickness of the metal, based
on the weight per unit area and an expected density of
7.7 g/cm^3, was 4.7 mm (0.18 in). The thicknesses measured
on the sawn edges varied from 3 to 7 mm (0.12 to 0.28 in).

While the specimens were in the various solutions, the
corrosion observed varied from very slight localized attack
to severe rusting. Table 3 gives the results of these cor-
rosion tests. The Table is divided into three sections,
the first for the specimens kept in the same solutions for
the duration of the experiments, the second and third for
the four specimens which were transferred to other solutions.

5

Table 3

Preservation of MONITOR Specimens by Various Solutions

Specimen Identification	Inhibitor (1) wt %	Trisodium Phosphate wt %	Preservation Rank (2)	Weight Loss g	Nature of Corrosion
Descaled, 119 days					
8	B 0.1	0.5	2.7	0.005	Local, slight
5	0	0.5	5.4	0.025	Local, plus small amount rust
6	N 0.1	0.5	5.4	0.04	Local
3	N 0.1	0	8.7	0.075	Rust, large amount plus local
1	B 0.1	0	9.0	0.155	Rust, large amount
2	B 0.5	0	9.2	0.175	Rust, large amount
With scale, 119 days					
11	N 0.1	0.5	1.3	0.01	Almost none
12	B 0.1	0.5	3.4	0.01	Local, slight
10	0	0.5	3.9	-0.02	Local, slight
9	N 0.5	0	5.9	0.105	Solution dark
Descaled, 6 days					
13	0	0	1	-	Rust, large amount, plus blackening
4	N 0.5	0	2	-	Rust, large amount

(continued)

(Table 3, continued)

Specimen Identification	Inhibitor (1) wt %	Trisodium Phosphate wt %	Preservation Rank (2)	Weight Loss g	Nature of Corrosion
With scale, 6 days					
14	0	0	3	--	Blackening
7	B 0.5	0	4	--	Blackening
Descaled, 113 days					
4	N 0.5	0.5	2.9	--	Local, slight
13	B 0.5	0.5	3.7	--	Local, slight
With scale, 113 days					
7	B 0.5	0.5	1.6	--	Almost none
14	N 0.5	0.5	1.9	--	Solution dark

(1) B = Sodium benzoate, N = Sodium nitrite.

(2) Lowest = best.

Each section is subdivided to separate the results with the descaled specimens from those with scale. The preservation rankings are interrelatable within sections, and are the averages of many rankings made during the experiment. These were subjective, based on the appearance of corrosion products on the specimens or in the solutions, and the lower numbers indicate less corrosion.

The most extensive and general rusting occurred with the descaled specimens in water and in inhibitor solutions without pH control. The specimens with scale in these same solutions blackened, probably due to sulfide formation. Trisodium phosphate alone was fairly effective, allowing only slight rusting and local corrosion. Both the benzoate and nitrite were effective when combined with trisodium phosphate. The solutions usually remained clear, and only traces of rust and slight localized corrosion forming black deposits were observed. The inhibitors were most effective at concentrations of 0.5%, although 0.1% was sufficient in most cases. For higher chloride concentrations, 1% might be necessary.

The benzoate solutions, which initially were slightly alkaline at a pH of 9, rapidly changed to a slightly acidic pH of 6. The nitrite solutions became gradually more alkaline, changing from a pH of 8 to about 9.5-11. The distilled water became the most acidic at pH = 5.5, but this is typical for water in equilibrium with atmospheric carbon dioxide. All solutions containing trisodium phosphate initially had a pH of about 11.5, which slowly decreased to as low as 9.7. Most surprising of these results was the relatively high pH of the unbuffered nitrite solutions, which did not inhibit corrosion even though their pH's were similar to those of the effective solutions buffered with phosphate. It is likely that pH in these solutions is not representative of conditions close to the metal surface where the corrosion is taking place. When checking the pH of a preservative solution, therefore, it is wise to also check the buffer strength by adding a small amount of acid and noting whether it reduces the pH drastically or only slightly. Other chemicals which can be used to maintain the alkalinity of preservative solutions include sodium hydroxide and sodium carbonate. Sodium hydroxide has little buffering ability and must be added frequently to replace that which is neutralized by reaction with atmospheric carbon dioxide. Sodium carbonate may form precipitates with calcium and magnesium from seawater salts.

Sulfide formation was seen in several instances, usually on the specimens with scale, and persisted through the entire study with specimens 9 and 14. The solutions were dark, and

8

the corrosion products on the specimens were black or dark brown. The corrosive attack on the metal was not great despite the drastic changes in appearance.

The extraction of chlorides from the specimens was, except for Nos. 9 and 14, successfully monitored with the specific ion electrode. As previously mentioned, the principal difficulty was interference by sulfide ions, most often involving the specimens with scale. The sulfides lowered the potential of the electrode, thus falsely indicating a high chloride concentration. Severe interference was characterized by failure of the potential to return to its previous level when the electrode was rinsed and placed in distilled water or standard chloride solutions. Minor interference, however, might have affected the chloride measurements without being apparent.

The chloride concentrations in the solutions increased rapidly at first, and then more and more slowly as the specimens became depleted. After the first few days, the chloride extractions followed the relationship:

$$C_o - \Sigma C = b \cdot 10^{mt}$$

where C_o was the amount of extractable chloride originally in the specimen, ΣC was the total amount extracted, and $(C_o - \Sigma C)$ was the remaining extractable chloride, all expressed as the weight of sodium chloride (NaCl), b and m were constants, and t was the time in hours. Plots of log $(C_o - \Sigma C)$ vs time thus fit straight lines of intercept log b and slope m, typical of a first-order rate process. The values of C_o, the initial chloride contents, were found by using a programmable calculator to automatically search for the values which produced the maximum correlation coefficients, which ranged from 0.948 to 0.993. The plots gave values for the initial extractable chloride contents and the amounts remaining at all times during the extractions.

Some representative plots are shown in Figs. 1-4. At the lower edge, below 0.1 mg NaCl, the analytical technique could not adequately detect the small changes in chloride concentration. The data usually followed the calculated line down to this region, but there was often a levelling of the extraction rate above 2000 hours, as seen in Figs. 2 and 4.

The results of these statistical analyses are given in Table 4. The data for final ΣC include the chlorides found in the rinses after atmospheric exposure. The computed values of C_O are in reasonable agreement with the total amount of chloride found, ΣC. In the majority of cases where there was disagreement, more chloride was found than was predicted. This indicates that there were impermeable pockets of chlorides which were not extractable until the pockets were ruptured by drying or subsequent corrosion. The intercepts of the plots indicate the amount of extractable chlorides within the porous structures. The differences between the intercepts and original concentrations C_O were due to superficial chlorides, which were removed in the first few days. The descaled specimens generally contained less chloride than those with scale, as would be expected.

Unfortunately, the potentially most useful result, the amount of chloride remaining after a given period of extraction, did not correlate well with the stability of the specimens in atmospheric exposure or the amount of additional chloride found in rinses afterward. The amount of occluded chloride which broke out was usually small in comparison with the amount originally present. However, it was often large in comparison with the amount of extractable chloride remaining, making this information less useful.

In addition to containing less chlorides, the descaled specimens released them more rapidly than those with scale in most cases. The last two columns in Table 4 give the first-order rate constants and the half-lives, both of which depend on the slopes of the extraction plots. The higher the rate constant, the more rapid the extraction. The half-life is the length of time required to reduce the extractable chloride content of a specimen to one-half of any previous level. The corrosion inhibitors had no clear effect on the rate of release. Although some of the more effective ones had higher rates, some of the specimens which rusted proved to be more stable in atmospheric exposure. Rusting may have promoted the release of chlorides, which otherwise would have remained occluded, by further oxidizing and removing the scale in which it was trapped. For example, among the descaled specimens, Nos. 2, 1, and 3 rusted the most during extraction (Table 3). These three had the lowest rate constants, and were also the only ones having ΣC less than C_O (Table 4). Numbers 1 and 2 were among the most stable in subsequent atmospheric exposure. The extractions of the other specimens probably would have been similar to these three if their occluded chlorides had been released by rusting or perhaps alternate wet and dry cycling.

10

Table 4

Regression Analysis of the Chloride Extractions

| Speci-men | Chloride, as wt.NaCl, mg | | | Rate Constant | Half-Life, Hours |
	ΣC Found, Final	C_o Calcu-lated	b Inter-cept	k $10^{-8}sec^{-1}$	
Descaled					
4	43.8	43.2	22.2	100	190
3	14.8	19.9	13.9	12	1670
6	19.8	17.0	9.6	30	640
2*	9.3	12.6	8.2	7.5	2570
8	10.6	10.5	5.6	27	700
5	12.1	10.4	4.9	43	450
1	3.8	4.2	2.8	12	1640
13*	10.1	3.8	3.0	59	330
With Scale					
7	59.4	71.3	39.7	10	1970
10	46.5	35.8	28.1	7.8	2480
12	48.0	30.2	22.7	12	1670
11	22.9	14.8	9.3	20	960

* Data base 93 to 2850 hrs. Others 93 to 1850 hrs.

Exposure of the extracted specimens to an atmosphere of 81% relative humidity produced changes which varied from the growth of small black or rusty spots on the surface to the exudation of deliquescent chloride salt solutions and continued corrosion of the wet metal. Most of the descaled specimens were relatively stable during the 43 days of exposure, as would be expected from their lower initial chloride contents. When exudation and corrosion were seen, they were associated with scale not completely removed by the acid descaling. Most of the specimens with scale collected droplets or puddles of liquid, and were removed after only 15 days. The extent of deterioration seen after 15 and 43 days correlated well with the amount of chloride found in the rinses after atmospheric exposure, indicating that the corrosion was due to chlorides released during this period.

11

After exposure to ambient conditions for 200 days, the specimens showed corrosion ranging from slight, powdery rust, not unexpected on unprotected iron, to exfoliating sheets of rust. Again, the descaled specimens were more stable than those with scale.

CONCLUSIONS

Hull plate samples from the MONITOR containing seawater salts were effectively preserved by nitrite and benzoate rust inhibitor solutions with trisodium phosphate. However, stabilization by extraction of the chlorides was not complete unless essentially all of the accretion and scale were removed first. Extraction of the accessible chlorides followed a first-order relationship. Additional chlorides remained in the scale until it was disrupted by drying or further oxidation.

For the temporary preservation of small ferrous metal objects which are to be reduced electrolytically or with hydrogen, the inhibitor solutions are recommended. Tap water or distilled water may be used, with between 0.1 and 1 percent by weight sodium nitrite ($NaNO_2$) or sodium benzoate, depending on the amount of chloride salts present, with 0.5% trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$). A few parts per million of a biocide such as Sodium Omadine (available from Olin Chemicals, 120 Long Ridge Road, Stamford, Conn., 06904) may be necessary to prevent bacterial growth and sulfide formation. This biocide is deactivated by light, and therefore poses no environmental problem upon disposal.

For the stabilization of objects too large for reduction, removal of the accretion and scale is necessary, followed by soaking in water to remove residual chloride salts. Thermal cycling or alternately drying and soaking might aid the release of occluded salts. The use of rust inhibitors in the water would prevent the unnecessary loss of metal, improve the appearance of the surface, and help to keep the solution clear so that local corrosion could be seen and treated. Measurements of the chloride concentration are useful in following the progress of the extraction.
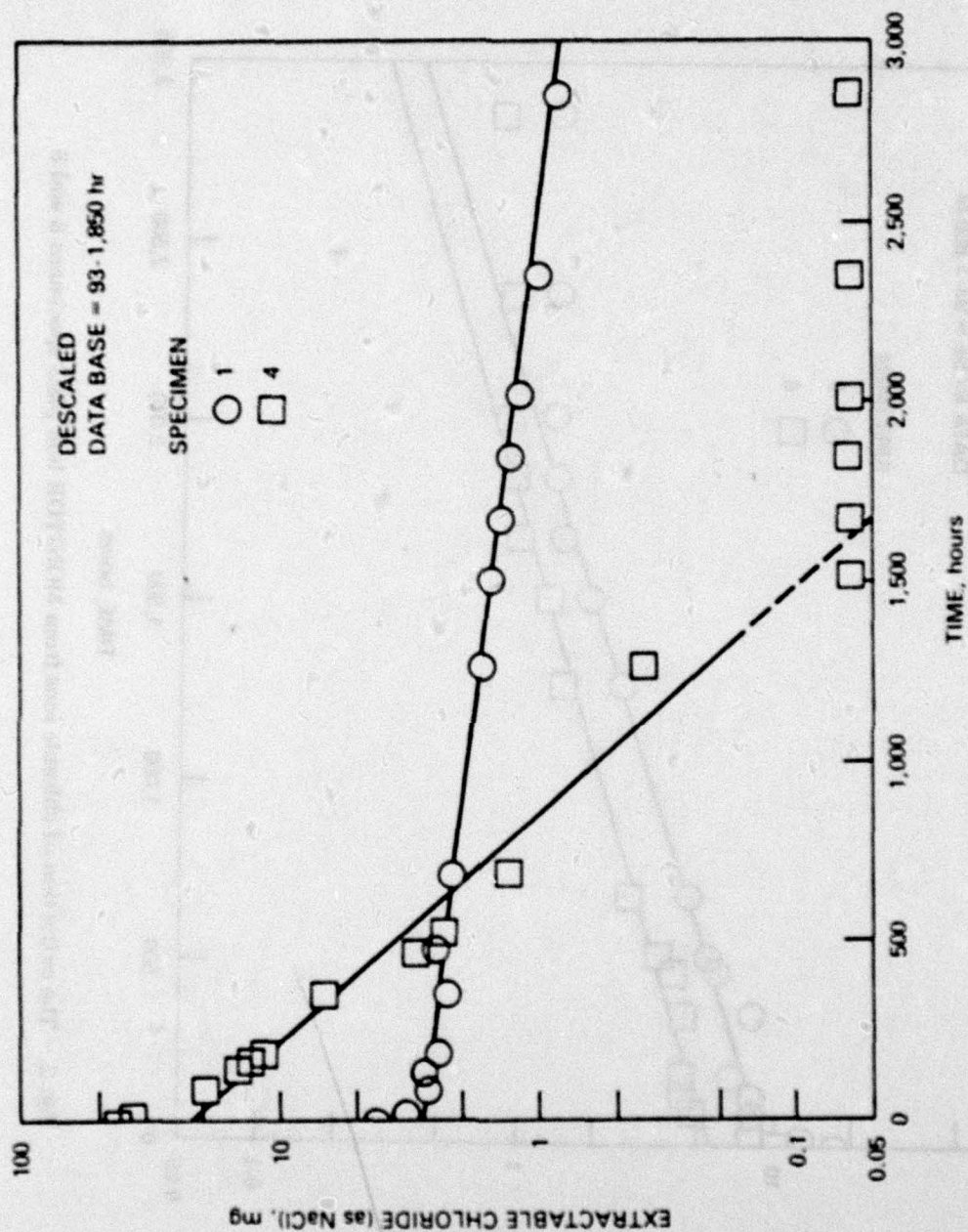
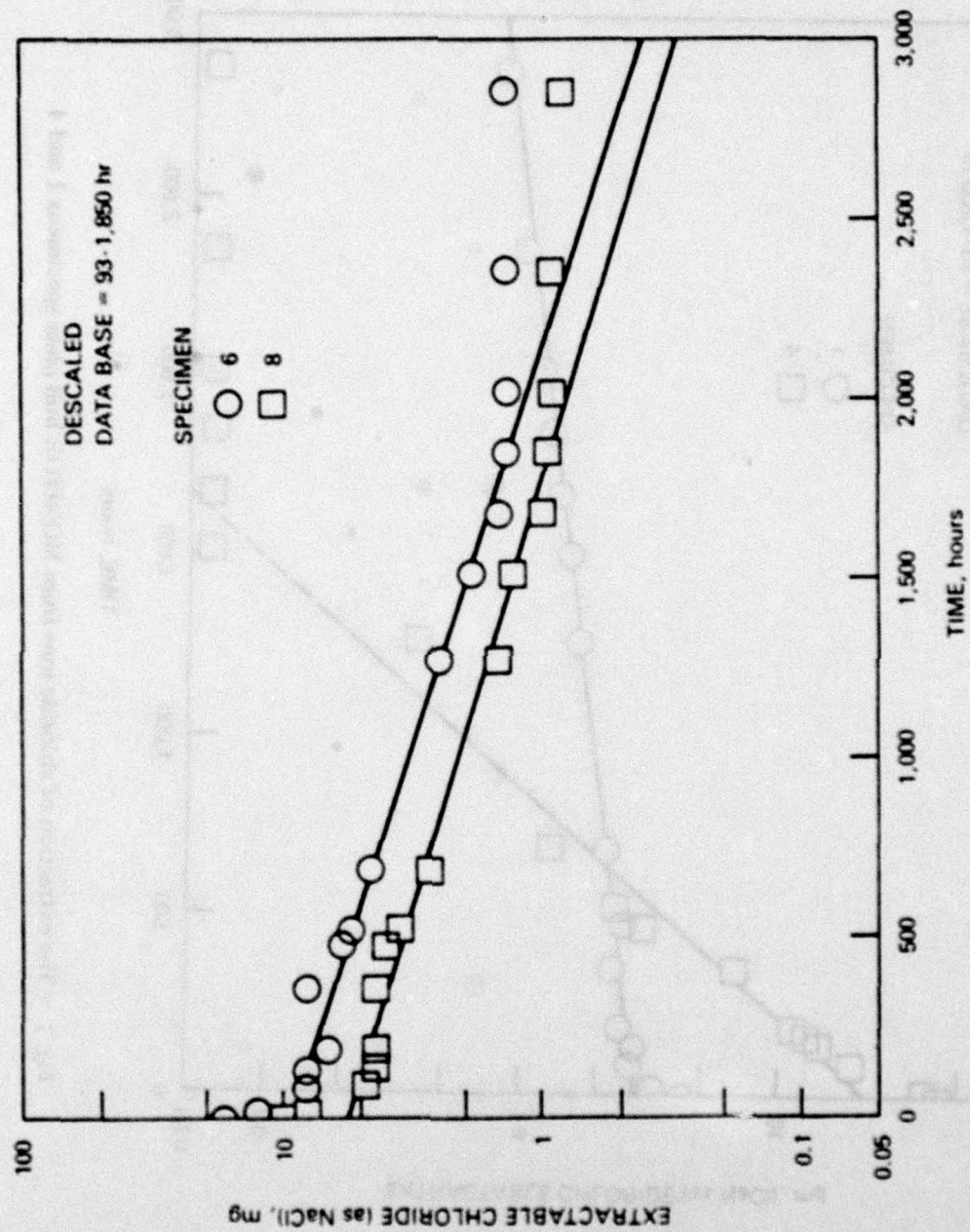Fig. 1 — The extraction of chloride ions from MONITOR hull plate specimens 1 and 4

13

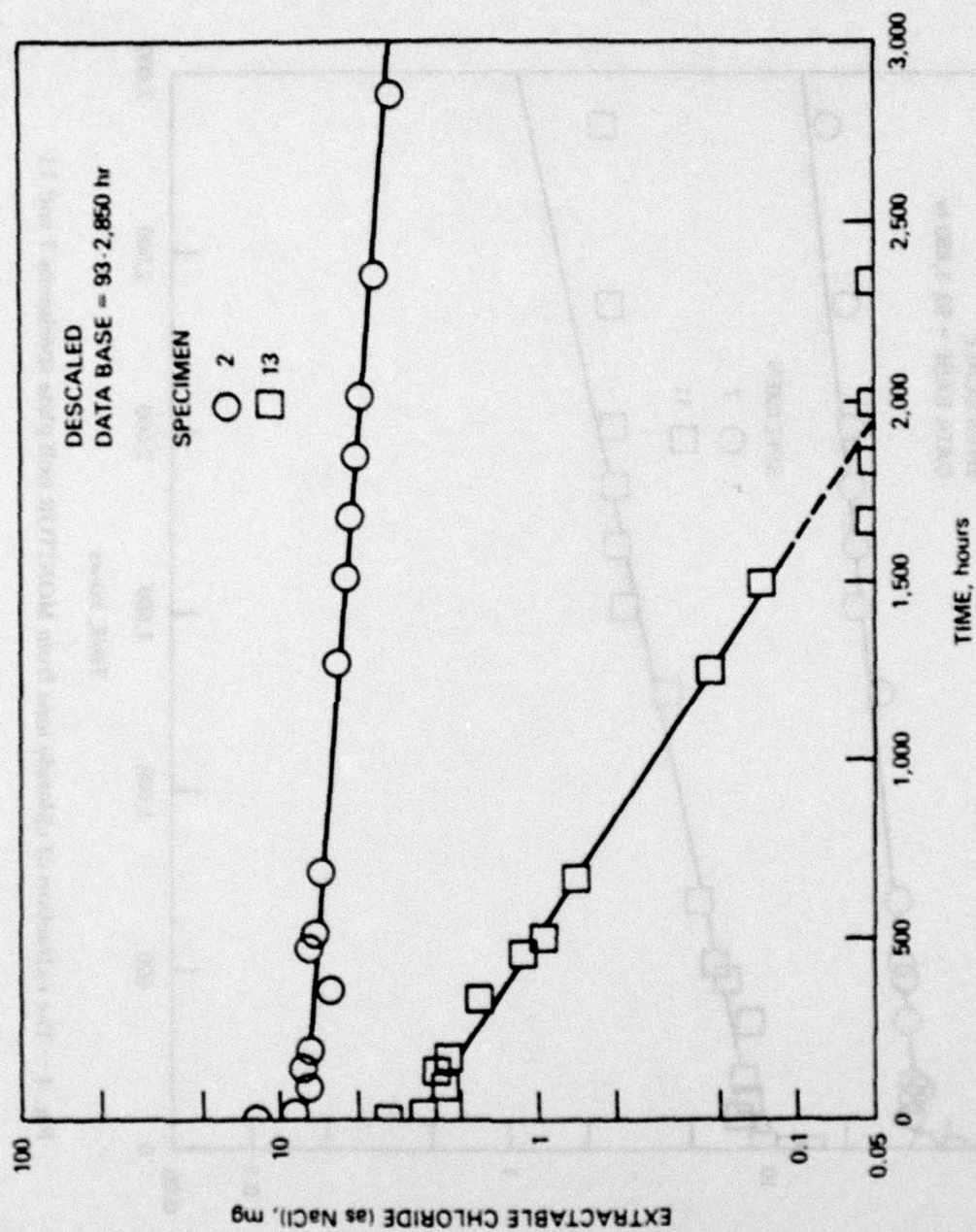Fig. 2 — The extraction of chloride ions from MONITOR hull plate specimens 6 and 8

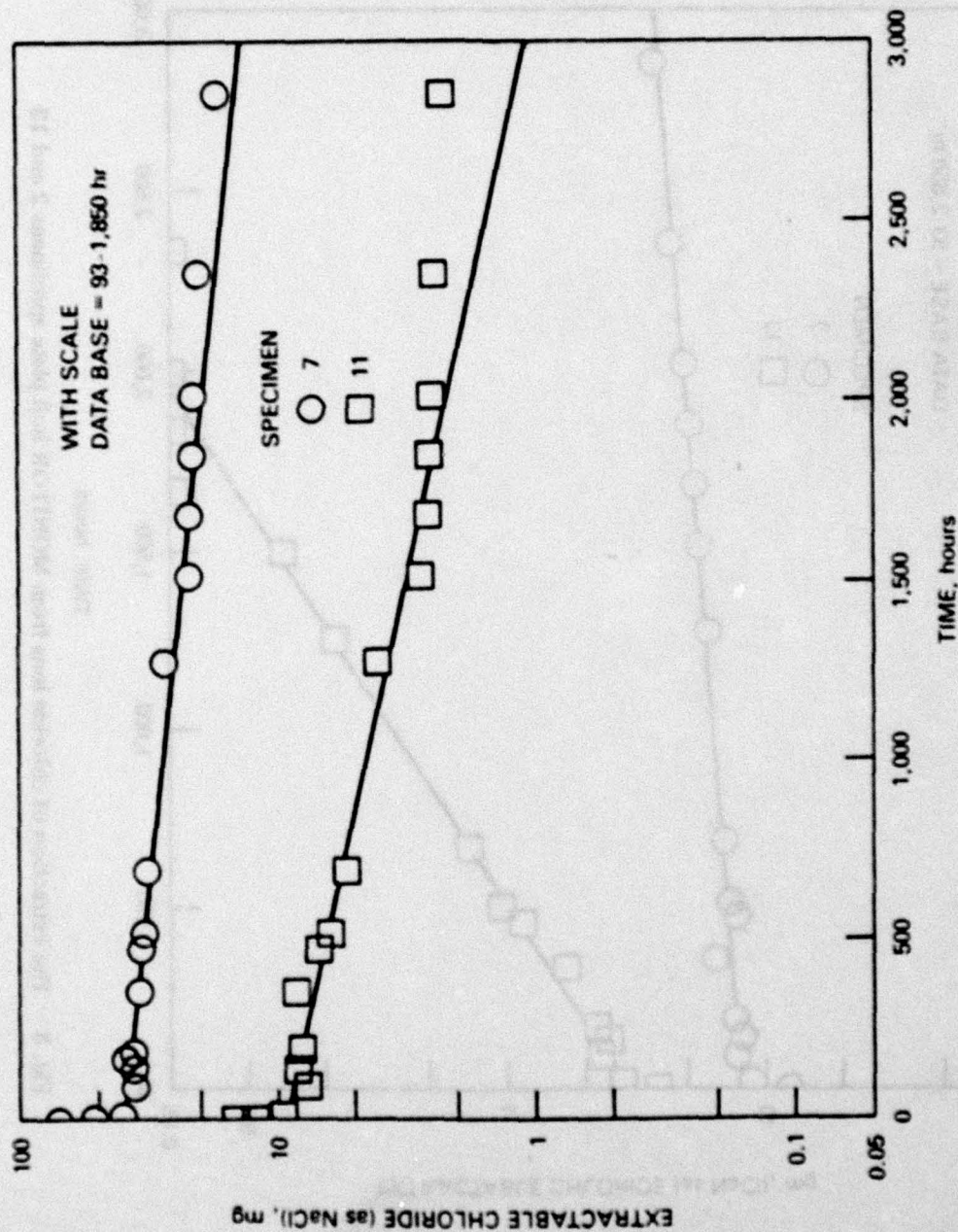Fig. 3 — The extraction of chloride ions from MONITOR hull plate specimens 2 and 13

15

Fig. 4 — The extraction of chloride ions from MONITOR hull plate specimens 7 and 11